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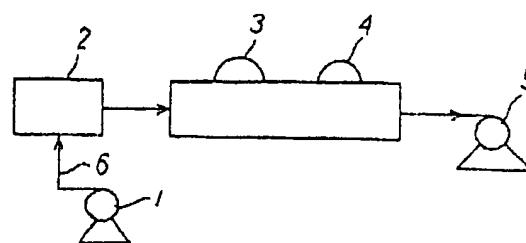
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Ukyo-ku, Kyoto, Japan(54) Title of the Invention: Method for forming a surface-protective layer
on food packaging materials

(57) Abstract

[Problem] To provide a method for forming a surface-protective layer on food packaging materials, wherein said method enables high-speed treatment in a small installation area.

formation of a safe surface-protective layer on the food packaging stock by high-speed treatment in a small installation area.

[Solution] Using a coater 2, the surface of food packaging stock 6 from an unwinder 1 is coated with an electron beam-curable coating. This coating is first cured by exposure to an electron beam in electron beam irradiator 3 and is thereafter exposed to UV radiation in UV irradiator 4 in order to treat the residual monomer from electron beam exposure. This enables utilization of the electron beam — which is capable of high curing reaction rates — and makes possible the



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Claim

[Claim 1] Method for forming a surface-protective layer on food packaging materials, said method being characterized by applying an electron beam-curable coating on a food packaging material, curing said coating by exposure to an electron beam, and treating the residual monomer by exposure to ultraviolet radiation.

Detailed Description of the Invention

[0001]

Field of the Invention

This invention relates to a method that uses an electron beam-curable coating to form a surface-protective layer on food packaging materials.

[0002]

Description of the Prior Art

During the utilization of food packaging materials, content descriptors and graphic elements are printed on the surface of the packaging stock and a transparent protective layer is then formed thereon. This protective layer is elaborated not only to protect the printed indicia, but also to enhance the gloss, scratch resistance, and wear resistance of the food packaging material. These protective layers have heretofore been formed by the so-called thermosetting method, in which a thermosetting

coating is applied on the stock surface and then dried by heating.

[0003]

Problems to Be Solved by the Invention

One problem with the thermosetting method is the long period of time required in order to cure the applied coating. This necessitates, in the case of mass production, a long and large drying oven, which in turn causes high equipment costs and requires a wide installation area. UV-curing and electron beam-curing technologies, which have recently undergone rapid development, have been contemplated as film curing technologies that would address these issues.

[0004]

UV-curing technology, while capable of relatively high-speed treatment in small installation areas at low equipment costs, nevertheless provides small irradiation energies and therefore requires that curing be carried out with the addition of a photoreaction initiator. This photoreaction initiator remains in the cured film, and its toxicity — and in some cases the evolution of an undesirable smell — are serious drawbacks to the use of the resulting coating for food packaging materials. These drawbacks prevent the use of UV-curing technology without some adaptation.

[0005]

Electron beam-curing technology is capable of even higher treatment speeds than UV-curing technology, and also uses a small installation area. Moreover, since this technology does not require the addition of a

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photoinitiator for curing, it could perhaps be considered as optimally qualified for application to food packaging materials. However, the curing reaction proceeds in a very short period of time in the case of electron beam curing, and monomer can remain in the cured product — although in very small amounts — as a consequence of nonuniformities in electron beam exposure. In such cases, the product cannot meet the potassium permanganate consumption requirement (elution test method) imposed by the Shokuhin-eisei-ho (the [Japanese] Food Sanitation Act)

[0006]

An excess electron beam exposure must be carried out in order to completely extinguish the residual monomer. This excess exposure is, however, not only uneconomical, but produces a cured film that is overpolymerized when considered from a quality standpoint. Such a film suffers from a number of problems: among others, it is hard and will crack when subjected to even gentle bending. It is therefore quite difficult to devise a suitable electron beam exposure level in the case of electron beam-curing technology.

[0007]

This invention was developed in view of the problems described above, and takes as its object the introduction of a method for forming a surface-protective layer on food packaging materials that enables high-speed treatment in a small installation area.

[0008]

Means Solving the Problems

The object of the invention is achieved by a method for forming a surface-protective layer on food packaging materials, said method being characterized by applying an electron beam-curable coating on a food packaging material, curing said coating by exposure to an electron beam, and treating the residual monomer by exposure to ultraviolet radiation.

[0009]

According to the characteristic features of this invention, since exposure to UV radiation is carried out in the presence of the unreacted free radicals that remain immediately after electron beam exposure, reaction can be promoted by the UV radiation — which is much less energetic than the irradiated electron beam — in the absence of a photoinitiator. This achieves a reduction only in the residual monomer from electron beam exposure with almost no change in the physical properties of the cured film. Thus, the electron beam and UV radiation, which are both capable of high curing reaction rates, can be used in combination to enable the high-speed production in a small installation area of a safe surface-protective layer on food packaging materials.

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[0010]

Embodiments of the Invention

Examples of the inventive method for forming a surface-protective layer on food packaging materials will be explained in detail in the following. Figures 1 through 3 contain structural diagrams of apparatuses usable by the inventive method for forming a surface-protective film. In Figures 1 through 3, **1** refers to an unwinder, **2** refers to a coater, **3** refers to an electron beam irradiator, **4** refers to an ultraviolet irradiator, **5** refers to a take-up apparatus, and **6** refers to the food packaging stock.

[0011]

Figure 1 depicts a configuration in which the electron beam irradiator and UV irradiator area are combined into a single unit and the food packaging stock is continuously transported through this unit. Figure 2 depicts a configuration in which the electron beam irradiator and UV irradiator are set up as separate structures and the food packaging stock is brought into temporary contact with the air after electron beam exposure and is thereafter subjected to UV irradiation. Figure 3 shows a configuration in which the stock is temporarily wound up after electron beam exposure and is thereafter subjected to UV irradiation.

[0012]

The principles underlying this invention will be considered first. UV-curing technology requires the addition of a photoreaction initiator due, as mentioned above, to this technology's

low level of irradiated energy. This photoreaction initiator undergoes decomposition upon absorption of energy from the UV radiation with the production of radicals. These radicals act as initiation points and the polymerization reaction proceeds therefrom. Thus, polymerization reactions are not initiated when the photoreaction initiator is not present. However, unreacted free radicals remain immediately after electron beam exposure. The execution of UV irradiation in the time interval during which these free radicals remain enables the free radicals to assume the role of initiation points for the photoreaction in the absence of a photoinitiator. This reaction results in polymerization of residual monomer with itself with ensuing decline in the amount of residual monomer as the monomer is converted into polymer

[0013]

The lifetime of the free radicals produced by electron beam irradiation depends on the temperature: higher temperatures result in shorter lifetimes. Typically the population is depleted by half after 1 hour at room temperature, and a major fraction is extinguished after 7 hours. In addition, since free radicals readily react with oxygen, exposure of the film surface to an oxygen-rich atmosphere also results in depletion of the free radicals in the surface region and hence in a reduction in the reaction with residual monomer.

[0014]

However, electron beam irradiators are designed to implement electron beam irradiation under a nitrogen (inert gas) atmosphere in order during the film cure operation to prevent ozone

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generation by reaction between the film and oxygen and collisions between the electron beam and oxygen. The interior of the irradiator therefore resides under a very oxygen-poor state.

[0015]

Therefore, in the optimal configuration, the surface of food packaging stock **6** from the unwinder **1** is coated by the coater **2** with an electron beam-curable coating; this coating is cured by exposure to an electron beam in the electron beam irradiator **3**; the residual monomer from electron beam exposure is then treated by exposure to UV radiation in a UV irradiator **4** that is integrated into a single unit with the electron beam irradiator **3**; and the treated food packaging stock **6** is wound up on the take-up apparatus **5**.

[0016]

In this configuration, exposure to UV radiation is carried out immediately after electron beam exposure, and the free radicals therefore have no opportunity to react with oxygen during the interval from completion of electron beam exposure to completion of UV exposure. This affords the most effective depletion of residual monomer since the reaction of residual monomer in the surface region is not inhibited.

[0017]

The stock making up the food packaging material can be a monolayer or composite sheet or tube of, for example, polyvinyl chloride, polyethylene, polypropylene, polystyrene, polyvinylidene chloride, nylon, or polyethylene terephthalate.

[0018]

The electron beam-curable coating can be, for example, monomer or oligomer containing at least 1 acryloyl group as its functional group; these are generally known as acrylic monomer.

[0019]

Monofunctional acrylic monomer can be exemplified by 2-ethylhexyl acrylate, 2-ethylhexyl-EO adduct acrylate, 2-phenoxyethyl acrylate, and phenoxydiethylene glycol acrylate.

[0020]

Disfunctional acrylic monomer can be exemplified by ethylene glycol diacrylate, polyethylene glycol diacrylate, and tripropylene glycol diacrylate.

[0021]

Trifunctional and higher functional acrylate monomer can be exemplified by trimethylolpropane triacrylate, ditrimethylolpropane tetraacrylate, dipentaerythritol hexaacrylate, dipentaerythritol-caprolactone adduct hexaacrylate, and trifunctional and higher functional oligoesters, urethane-type oligomers, and epoxy-type oligomers.

[0022]

With regard to electron beam irradiation, the electron beam acceleration voltage should be from 100 to 3,000 kV and the dose should be from 0.1 to 30 Mrad, while the acceleration voltage is preferably from 150 to 300 kV and the dose is preferably from 1 to 15 Mrad. The irradiation atmosphere should be an inert gas atmosphere, such as nitrogen, in which the residual oxygen concentration is preferably no more than 500 ppm.

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[0023]

UV irradiation can be carried out from an apparatus that has a source (typically a high-pressure mercury lamp or metal halide lamp) that produces UV radiation with a wavelength from 200 to 450 nm. The UV dose should be at least 30 mJ/cm² and is preferably at least 50 mJ/cm².

[0024]

The gap between electron beam exposure and UV exposure is preferably traversed as rapidly as possible, and during this traverse the film surface preferably does not come into contact with air. Given these preferred features, the method shown in Figure 1 for forming the surface-protective film is optimal. However, as shown in Figure 2, in another possible embodiment UV exposure can be carried out immediately after electron beam exposure even with contact between the air and film surface. In yet another possible embodiment as shown in Figure 3, the film can be rapidly wound up immediately after electron beam exposure and held prior to UV exposure out of contact with air in order to prevent extinction of the free radicals by reaction with the air.

[0025]

Since radicals will be present — although in very small amounts — even after 1 day, initiation points for the photoreaction can be produced at this time as long as a large UV exposure dose is used. However, the use of large UV doses in such cases is uneconomical and also runs the risk of producing thermal deformation in the substrate depending on the particular type of substrate.

[0026]

Examples**Example 1**

This example used the apparatus whose structure is shown in Figure 1. The stock in this case was 50 μ m-thick polyethylene film that had been subjected to a corona treatment. The following mixed composition was coated thereon using a gravure coater so as to produce a coating thickness of 5 μ m:

- (1) 30 weight parts acryloylmorpholine (ACMO from Kojin KK),
- (2) 40 weight parts tripropylene glycol diacrylate (Aronix M-220 from Toa Gosei Kagaku Kogyo KK), and
- (3) 30 weight parts dipentaerythritol-caprolactone adduct hexaacrylate (Kayarad DPCA-60 from Nippon Kagaku KK).

[0027]

After the coating operation, the film was cured using an area beam-type electron beam irradiator. This curing was run in a nitrogen atmosphere using an acceleration voltage of 150 kV and a dose of 10 Mrad. Curing was followed immediately by exposure in the UV irradiator at 10, 30, or 50 mJ/cm². The resulting films were tested for their potassium permanganate consumption using the elution testing methodology in the Food Sanitation Act, and the following values were obtained.

10.8 ppm at 10 mJ/cm²
5.2 ppm at 30 mJ/cm²
2.0 ppm at 50 mJ/cm²

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[0028]

Example 2

This example used the apparatus whose structure is shown in Figure 2. The stock in this case was 50 μm -thick polyethylene film that had been subjected to a corona treatment. The following mixed composition was coated thereon using a gravure coater so as to produce a coating thickness of 5 μm :

- (1) 30 weight parts acryloylmorpholine (ACMO from Kojin KK),
- (2) 40 weight parts tripropylene glycol diacrylate (Aronix M-220 from Toa Gosei Kagaku Kogyo KK), and
- (3) 30 weight parts dipentaerythritol-caprolactone adduct hexaacrylate (Kayarad DPCA-60 from Nippon Kagaku KK).

[0029]

After the coating operation, the film was cured using an area beam-type electron beam irradiator. This curing was run in a nitrogen atmosphere using an acceleration voltage of 150 kV and a dose of 10 Mrad. Curing was followed immediately by exposure in the UV irradiator at 10, 30, or 50 mJ/cm^2 . The resulting films were tested for their potassium permanganate consumption using the elution testing methodology in the Food Sanitation Act, and the following values were obtained.

13.5 ppm at 10 mJ/cm^2
10.6 ppm at 30 mJ/cm^2
3.7 ppm at 50 mJ/cm^2

[0030]

Example 3

This example used the apparatus whose structure is shown in Figure 3. The stock in this case was 50 μm -thick polyethylene film that had been subjected to a corona treatment. The following mixed composition was coated thereon using a gravure coater so as to produce a coating thickness of 5 μm :

- (1) 30 weight parts acryloylmorpholine (ACMO from Kojin KK),
- (2) 40 weight parts tripropylene glycol diacrylate (Aronix M-220 from Toa Gosei Kagaku Kogyo KK), and
- (3) 30 weight parts dipentaerythritol-caprolactone adduct hexaacrylate (Kayarad DPCA-60 from Nippon Kagaku KK).

[0031]

After the coating operation, the film was cured using an area beam-type electron beam irradiator. This curing was run in a nitrogen atmosphere using an acceleration voltage of 150 kV and a dose of 10 Mrad. After holding for 5 hours, exposure in the UV irradiator was then run at 50, 100, or 200 mJ/cm^2 . The resulting films were tested for their potassium permanganate consumption using the elution testing methodology in the Food Sanitation Act, and the following values were obtained.

13.4 ppm at 50 mJ/cm^2
9.5 ppm at 100 mJ/cm^2
6.3 ppm at 200 mJ/cm^2

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[0032]

Example 4

This example used the apparatus whose structure is shown in Figure 3. The stock in this case was 50 μm -thick polyethylene film that had been subjected to a corona treatment. The following mixed composition was coated thereon using a gravure coater so as to produce a coating thickness of 5 μm :

- (1) 30 weight parts acryloylmorpholine (ACMO from Kojin KK),
- (2) 40 weight parts tripropylene glycol diacrylate (Aronix M-220 from Toa Gosei Kagaku Kogyo KK), and
- (3) 30 weight parts dipentaerythritol-caprolactone adduct hexaacrylate (Kayarad DPCA-60 from Nippon Kagaku KK).

[0033]

After the coating operation, the film was cured using an area beam-type electron beam irradiator. This curing was run in a nitrogen atmosphere using an acceleration voltage of 150 kV and a dose of 10 Mrad. After holding for 1 day, exposure in the UV irradiator was then run at 200, 500, or 1,000 mJ/cm^2 . The resulting films were tested for their potassium permanganate consumption using the elution testing methodology in the Food Sanitation Act, and the following values were obtained:

29.4 ppm at 200 mJ/cm^2 , no deformation
17.3 ppm at 500 mJ/cm^2 , deformation occurred
7.4 ppm at 1,000 mJ/cm^2 ,
deformation occurred

[0034]

Comparative Example 1

This example used an apparatus composed of only an electron beam irradiator. The stock in this case was 50 μm -thick polyethylene film that had been subjected to a corona treatment. The following mixed composition was coated thereon using a gravure coater so as to produce a coating thickness of 5 μm :

- (1) 30 weight parts acryloylmorpholine (ACMO from Kojin KK),
- (2) 40 weight parts tripropylene glycol diacrylate (Aronix M-220 from Toa Gosei Kagaku Kogyo KK), and
- (3) 30 weight parts dipentaerythritol-caprolactone adduct hexaacrylate (Kayarad DPCA-60 from Nippon Kagaku KK).

[0035]

After the coating operation, the film was cured using an area beam-type electron beam irradiator. This curing was run in a nitrogen atmosphere using an acceleration voltage of 150 kV and a dose of 10, 30, or 50 Mrad. The resulting films were tested for their potassium permanganate consumption using the elution testing methodology in the Food Sanitation Act, and the obtained values are reported below. Also reported below are the results from 180° bending tests executed on the films.

38.2 ppm at 10 Mrad, no film cracking
18.9 ppm at 30 Mrad, no film cracking
8.7 ppm at 50 Mrad, film cracking occurred

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[0036]

The Food Sanitation Act specifies a value of ≤ 10 ppm for the potassium permanganate consumption measured using the Act's elution testing methodology. Example 1, which involved UV irradiation immediately after electron beam exposure, gave a value that satisfied the Food Sanitation Act at 30 mJ/cm^2 . Example 2 also involved UV irradiation immediately after electron beam exposure, but with contact with the air between the two treatments. In this case, 50 mJ/cm^2 was required to give a value that satisfied the Food Sanitation Act.

[0037]

Examples 3 and 4 employed a holding period of 5 hours and 1 day, respectively, between electron beam exposure and UV exposure. Values meeting the Food Sanitation Act were obtained when the UV dose was increased, but the higher doses were somewhat problematic because they caused film deformation to occur.

[0038]

Comparative Example 1 did not use UV irradiation, and as a result the values did not comply with the Food Sanitation Act up to and including 30 Mrad. Although a compliant value was obtained when the dose was raised up to 50 Mrad, film cracking was produced at this dose level.

[0039]

Advantageous Effects of the Invention

As has been described above, this invention can decrease elution of residual monomer from the cured film. The invention

achieves this as follows: after application of an electron beam-curable coating on food packaging material and cure of this coating by exposure to an electron beam, exposure to UV radiation is immediately carried out within the time interval in which unreacted free radicals still remain in situ. The decreased residual monomer elution enables compliance with the potassium permanganate consumption by elution testing that is stipulated in the Food Sanitation Act. This enables utilization of electron beam technology, with its capacity for high curing reaction rates, and enables the formation of a safe surface-protective layer on food packaging materials at high treatment speeds and in small installation spaces.

Brief Description of the Drawings

Figure 1 contains a structural drawing of one example of an apparatus that can be used by the method according to the present invention for forming surface-protective layers.

Figure 2 contains a structural drawing of another example of an apparatus that can be used by the method according to the present invention for forming surface-protective layers.

Figure 3 contains a structural drawing of yet another example of an apparatus that can be used by the method according to the present invention for forming surface-protective layers.

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[Reference Symbols]

1	-----	unwinder
2	-----	coater
3	-----	electron beam irradiator
4	-----	UV irradiator
5	-----	take-up apparatus
6	-----	food packaging stock

Figure 1.

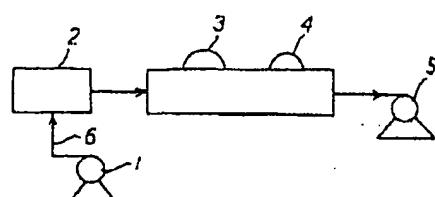


Figure 2.

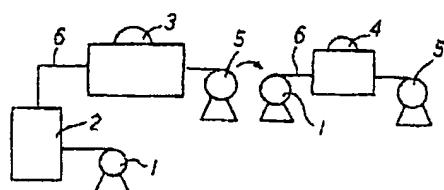
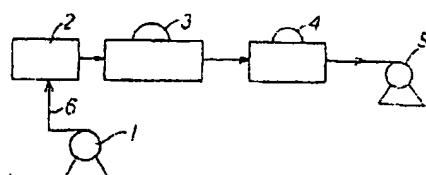


Figure 3.